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Potential for analysis of carbonaceous matter on Mars using Raman spectroscopy

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ABSTRACT

The ESA/Roscosmos ExoMars rover will be launched in 2018. The primary aim of the mission will be to find evidence of extinct or extant life by extracting samples from the subsurface of Mars. The rover will incorporate a drill that is capable of extracting cores from depths of up to 2 m, a Sample Preparation and Distribution System (SPDS) that will crush the core into small grains and a suite of analytical instruments. A key component of the analytical suite will be the Raman Laser Spectrometer (RLS) that will be used to probe the molecular and mineralogical composition of the samples. In this work we consider the capability of the proposed Raman spectrometer to detect reduced carbon (possibly associated with evidence for extinct life) and to identify the level of thermal alteration/maturity. The Raman analysis of 21 natural samples of shale (originating from regions exhibiting different levels of thermal maturity) is described and it is shown that reduced carbon levels as low as 0.08% can be readily detected. It is also demonstrated that the Raman spectra obtained with the instrument can be used to distinguish between samples exhibiting high and low levels of thermal maturity and that reduced carbon can be detected in samples exposed to significant levels of oxidation (as expected on the surface of Mars).

1. Introduction

Raman spectroscopy has potential as a technique for in-situ analysis during planetary exploration (Jehlička et al., 2009; Wang et al., 2003; Rull et al., 2011). A significant advantage of the technique is that it can be applied to analyse both inorganic and organic components of rocks and soils (Jehlička et al., 2005, 2009; Jehlička and Edwards, 2008). Accordingly, it has been selected for inclusion in the 2018 ExoMars mission, a major objective of which is to search for evidence of life on Mars (Rull et al., 2011). A particularly important aspect of the instrument design, operation and associated spectroscopic analysis is the characterization of mineralogy, which is deemed favourable for the support of extinct life signatures.

Existing literature on the application of Raman spectroscopy to the search for evidence of life has focussed on the detection of complex organic compounds, such as pigments in suitable geological matrices (Edwards et al., 2012; Vítek et al., 2009a, 2009b). The selection of appropriate biomarkers in the geological record is currently the subject of investigation by various groups (e.g. Parnell et al., 2007). However, we are more likely to discover evidence for ancient, fossilized life on Mars, as opposed to extant life, and this is reflected in the exploration strategy for ExoMars (Vago et al., 2006). Fossilized life, possibly billions of years old, will be most evident as reduced carbon (sp^2 hybridized solid crystalline carbonaceous material), rather than complex molecules, at least in the abundance required for detection by Raman spectroscopy. Indeed, evidence for reduced carbon (a term used here to refer to sp^2 disordered carbon) on Mars has been recorded as veinlets of carbonaceous matter in the Nakhla meteorite (Gibson et al., 2006; McKay et al., 2006). Reduced carbon on Mars could have either a biotic or abiotic origin and indeed, has been related to infall of carbonaceous meteorites (Sephton, 2002). A recent study of martian meteorites has shown that most contain reduced carbon of magmatic origin (Steele et al., 2012). Raman analysis cannot be used to directly distinguish between carbonaceous material formed by abiogenic and biogenic processes (i.e. Pasteris and Wopenka, 2002, 2003; Marshall et al., 2010). To better understand

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potential biogenicity (as well as the autochtonous character of carbonaceous matter in Precambrian rocks), it has been suggested that complementary studies should be performed by including/integrating spectroscopic techniques with geological observations (van Zuilen et al., 2007; Tice et al., 2004; Olcott Marshall et al., 2012, 2014).

However, regardless of origin, the detection of reduced carbon on Mars would be a major step forward in the remote analytical exploration of the planet's surface and subsurface.

There is already a substantial database of Raman spectroscopic data that has been obtained from the analysis of reduced carbon in extraterrestrial samples, including meteorites (Bonal et al., 2006; Busemann et al., 2007) and cometary/interplanetary dust particles (Rotundi et al., 2008), as well as in ancient, terrestrial samples, such as Archean rocks (e.g., Marshall et al., 2007, 2010, 2011; Marshall and Olcott Marshall, 2011; Olcott Marshall et al., 2012; Olcott Marshall and Marshall, 2013), Proterozoic rocks (e.g., Jehlička and Rouzaud, 1990; Jehlička and Bény, 1992; Olcott Marshall et al., 2009) and Proterozoic microfossils (e.g., Arouri et al., 2000; Marshall et al., 2005; Dhamelincourt et al., 2010; Schiffbauer et al., 2012). Recent Raman spectroscopic investigations of carbonaceous materials in Archean rocks have led to the discovery that multiple populations of carbonaceous materials of vastly different thermal maturities exist in these rocks (e.g., Olcott Marshall et al., 2012; Lepot et al., 2013), hence suggesting different sources and timing for the origins of carbonaceous materials. Raman spectroscopy of Proterozoic microfossils reveals that they are composed of disordered sp^2 carbonaceous material that has structural organization that is consistent with the metamorphic grade experienced for that region. Although morphology indicates that these microfossils are clearly biogenic materials, Raman spectroscopy does not afford any information about the biopolymer composition or biogenicity of Proterozoic microfossils but rather elucidates the structural organization of carbon present within the microfossil (e.g., Marshall et al., 2005). Quirico et al. (2009) compared the Raman spectroscopic characteristics of a series of meteoritic carbons from chondrites and Palaeozoic coals of different origins. They highlighted the similarities and differences between features associated with the Raman spectral parameters of the carbon G and D bands (also see Pasteris and Wopenka, 2002, 2003; Marshall et al., 2010). The Raman spectra of sp^2 carbonaceous material, Polyaromatic Carbonaceous Matter (PCM), of 42 chondrites and 27 coal samples were measured with 244 nm excitation wavelengths as well as 514.5 nm (noting that the D band is dispersive and provides weak response in the UV and enhanced response in the red, but also that in the deep UV, minute quantities of sp^3 carbon bound within the sp^2 macromolecular network can be detected). The Raman spectra of low rank coals and chondrites of petrologic types 1 and 2, which contain the more disordered PCM, reflect the distinct carbon structures of their precursors. The 514 nm Raman spectra of high rank coals and chondrites of petrologic type 3 exhibit continuous and systematic spectral differences reflecting different carbon structures present during the metamorphism event. The results obtained suggest that the use of low temperature carbon thermometers should be restricted to a given geological context but, at the same time, the sensitivity of Raman spectra to precursors and certain metamorphic conditions could be used to obtain information other than temperature.

The evolution of Raman spectra related to changes in structural arrangement of carbonaceous matter during high temperature treatment (HTT) was first observed in the frame of laboratory experiments under inert atmospheres (Bény Bassez, 1985). Pasteris and Wopenka (1991) have demonstrated that the Raman spectra of graphitic material in rocks reflect the degree of crystallinity (L_a) in natural samples. They demonstrated that the Raman spectrum can be considered as a fingerprint of changes in the degree of graphitization in rocks related to the intensity of metamorphism. In a complex study, Wopenka and Pasteris (1993) investigated an important series of carbons (among other samples, 24 grain separates from various metamorphic terrains from chlorite zone to granulite facies). It was shown that the Raman shift positions, widths, intensity ratios, and area ratios of the Raman G and D bands evolved in correlation with the degree of ordering. The authors estimated the in-plane crystallite size, L_a, based on the existing calibration data (XRD). Several other authors have investigated how Raman spectra reflect changes during regional metamorphism at atomic and molecular level in rocks of different ages (Jehlička and Bény, 1992; Jehlička et al., 1997; Kříbek et al., 1994; Yui et al., 1996; Beyssac et al., 2002a, 2002b, 2003; Rantitsch et al., 2005). Beyssac et al. (2002a) found a linear correlation between $R2$ (the $D1/[G+D1+D2]$ area ratio) and metamorphic temperature which they calibrated using samples from different regional metamorphic belts with well-known P–T conditions and Kříbek et al. (1994) performed a detailed investigation of carbonaceous matter from Palaeoproterozoic black shales from the Birimian volcano-sedimentary belt (Burkina Faso, West Africa). In the latter study, Raman spectroscopy was used to complement the vitrinite reflectance measurements and the authors describe multiple types of carbonaceous particles in the investigated rocks, some of them affected by hydrothermal processes.

The potential for analysing reduced carbon with the Raman instrument intended for use on Mars during the ExoMars mission has not been extensively explored, yet it has the potential to deliver information important to the objectives of the mission. Consequently, in this study, we have selected a terrestrial dataset of specimens which will be used to evaluate instrument performance in the following three key areas: (i) detection of low contents of carbon, (ii) detection of carbon in samples that have experienced oxidation, which is pervasive on the martian surface (Zent, 1998), and (iii) detection of different degrees of thermal alteration, which would be valuable in informing which other analytical techniques on the mission could be deployed to investigate organic components. It is recognized that all of the specimens selected for analysis contain carbon from biotic sources.

2. Methodology

The primary aim of this study was to analyse (through blind testing) the Raman spectra of a large number of milled shales (21) in order to investigate the ability of the ExoMars Raman spectrometer to detect low concentrations (i.e. $< 0.1\%$) of reduced carbon and to differentiate between different levels of thermal maturity.

2.1. Samples

The shales were obtained from various locations in the Devonian Orcadian Basin in Caithness, northern Scotland. The basin contains a non-marine, mixed fluviatile–lacustrine succession, in which the lacustrine rocks contain organic matter, precipitated by algae (Donovan, 1975; Trewin, 1986). The thermal maturity of the organic matter varies from immature to overmature, i.e. they have released varying quantities of hydrocarbons in different areas (Hillier and Marshall, 1992). In particular there is a contrast in thermal maturity across a major lineament, the Brough Fault, where rocks to the west are thermally mature and rocks to the east are mature to overmature (Hillier and Marshall, 1992). A distinction into low, moderate and high levels of thermal maturity (according to the data in Hillier and Marshall, 1992) is shown in Fig. 1. The burial history of the rocks can be divided into three phases (Parnell et al., 1998): initial deposition of lacustrine siltstones, then burial during which the organic carbon